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D. Craig and L.M. Johnston

Ground Water Division
National Hydrology Research Institute
Environment Canada
Saskatoon, Saskatchewan
S7N 3H5

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# Acid Precipitation and Groundwater Chemistry at the Turkey Lakes Watershed

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D. Craig and L. M. Johnston

*National Hydrology Research Institute, Environment Canada, 11 Innovation Boulevard, Saskatoon, Sask. S7N 3H5*

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To determine correctly the response of a basin to various acid loading events, the groundwater hydrology must be considered as a function of the basin stratigraphy and mineralogy. Groundwaters in the Turkey Lakes Watershed are well buffered and in general provide a reservoir of alkalinity for surface waters in the basin. The groundwater chemistry is dominated by the weathering of carbonates present in the tills. Groundwater can follow a variety of pathways through the subsurface. These pathways can have very different flow rates and groundwater chemistry. As a result of this the influence of groundwater on surface water is highly site specific.

Afin de déterminer exactement la réaction d'un bassin versant à diverses charges acides, on doit considérer l'hydrologie des eaux souterraines comme fonction des caractéristiques stratigraphiques et minéralogiques du bassin versant. Les eaux souterraines du bassin versant des lacs Turkey sont bien ajustées à un pH donné et, en général, constituent un réservoir d'alcalinité pour les eaux de surface du bassin. La chimie des eaux souterraines est dominée par l'altération aux agents atmosphériques des carbonates présents dans les moraines de fond. Les eaux souterraines peuvent suivre une variété de cheminements sous la surface. Ces cheminements peuvent avoir des taux de débit et une chimie des eaux souterraines très variables. Par conséquent, l'influence des eaux souterraines sur les eaux de surface est très particulière à chaque site.

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Studies in the Turkey Lakes Watershed, located north of Sault Ste. Marie, Ontario, Canada (Fig. 1), are examining the effects of acidic precipitation on a string of five lakes in a forested, temperate watershed (Jefferies and Semkin 1982). This paper presents the results of a study of groundwater chemistry in the watershed and describes the dominant weathering reactions and processes that govern this chemistry, particularly as they relate to the problem of "acid rain." Normal weathering reactions are natural processes caused by autogenic carbonic acid and mineral acids. The addition, however, of large quantities of anthropogenic sulfur ($SO_4$) and nitrogen ($NO_4$) to the atmosphere and their subsequent deposition would be expected to modify (probably increase) natural rates of geochemical weathering. In areas such as the Turkey Lakes Watershed, where carbonates are present in the tills, neutralization of any acidic loading to the groundwater is ultimately due to the weathering of these carbonates. Where carbonates are not present, the weathering of aluminium hydroxides (gibbsite) and aluminum silicate minerals becomes important in consuming $H^+$.

Recent studies on acid rain have underlined the importance of the ability of a given terrain to neutralize acid loadings. The composition and structure of surficial deposits in a given watershed and the pathways that subsurface waters follow through such materials are important factors in watershed acidification (Bache 1984; Booty and Kramer 1984).

Chemical and isotopic studies of streamwater have shown that the major contribution to both baseflow and stormflow is through the groundwater system (Dincer et al. 1970; Fritz et al. 1976; Sklash and Farvolden 1979; Bottomley et al. 1984, 1986). Most of the water in a stream during a runoff event (i.e. rain and/or snowmelt) is pre-event water, that is, water that has been stored in the basin from previous events (Pearce et al. 1986). The mechanism underlying this process is not well understood. Most models of flow generation utilize the concept of recha and discharge areas for groundwater (Dunne 1983; Ragan 19 Van de Griend and Arwert 1983; Rodhe 1981). According these models, rain or snowmelt on the upper parts of a watersh infiltrates and raises the water table (influent or recharge area and this in turn increases the outflow of groundwater downslo in the valley floors (effluent or discharge areas). Overland fl occurs only in discharge areas, where the soil is saturated fr below (distinct from Hortonion overland flow; Horton 193 These areas of saturated overland flow are often referred to partial areas and are felt to be responsible for a large compon of stream storm runoff in some basins whereas subsurface fl dominates in others.

In conjunction with these groundwater movements, there two stages in the neutralization of acid loadings in the terrest component of the hydrologic cycle. In the initial stage, in trating precipitation or meltwater reacts rapidly in the upper s horizons. This results in a rapid rise in the pH of the infiltrati water. During the second, much longer stage, subsurface wa equilibrates with carbonate or silicate minerals in the overb den. The second stage can result in large increases in the bic bonate dissolved in the groundwater, bicarbonate which is th advected to the surface water through groundwater discharg Identifying the actual process by which streamflow is generat subsequent to a loading event is critical to a correct evaluati of a basin's sensitivity, since the degree of sensitivity depen on the water pathways through the subsurface. This is becau the water pathways determine the material that the water con in contact with during its passage through the terrestrial part the catchment. As the groundwater pathways largely determi the spatial distribution of the groundwater chemistry, it follo that by examining the spatial distribution of the groundwa

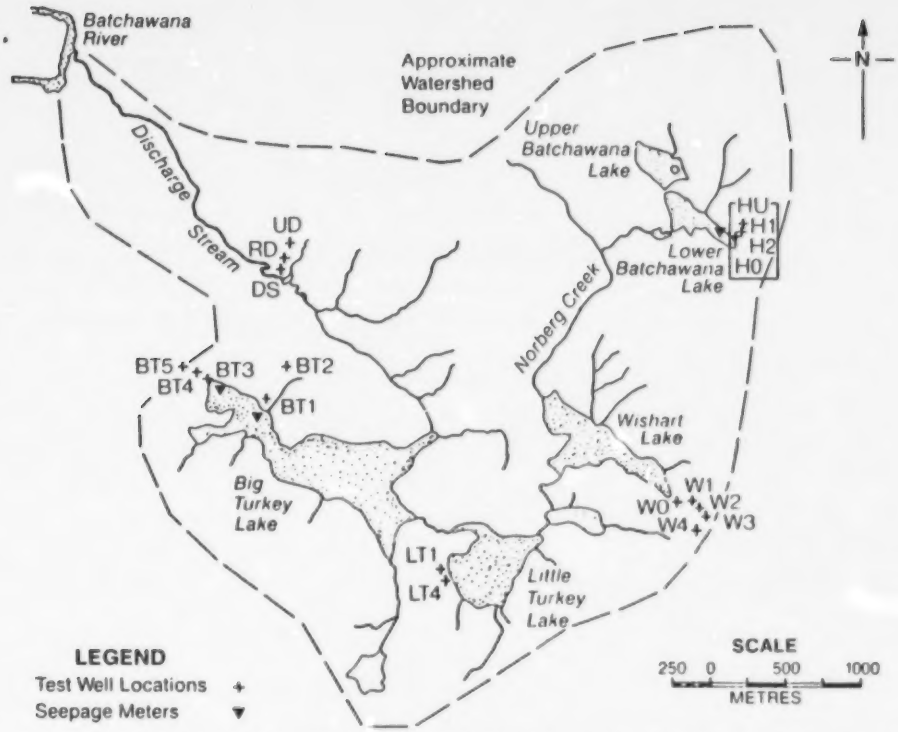


FIG. 1. Test well locations in the Turkey Lakes Watershed located north of Sault Ste. Marie, Ont.

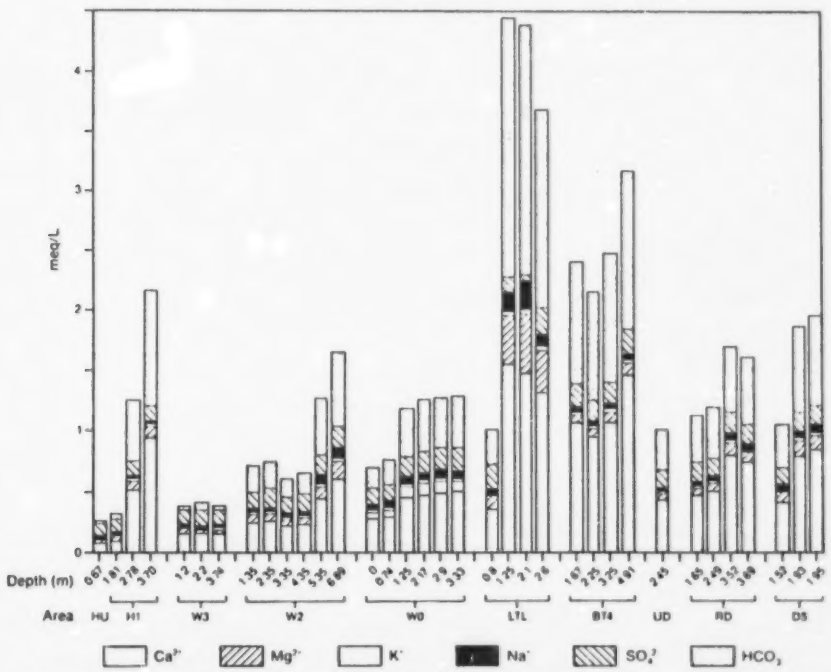


FIG. 2. Groundwater chemistry at the Turkey Lakes Watershed. Bar graph is grouped by piezometer nest, with increasing depth from left to right within the group.

chemistry, it is possible to make inferences about the groundwater flow system.

Prior studies at the Turkey Lakes and Harp Lake watersheds have underlined the ameliorative effects of groundwater in minimizing pH depression in surface waters during acid loading events (Bottomley et al. 1984, 1986).

## Site Description

The Turkey Lakes Watershed is subject to moderate to high atmospheric loadings of strong acids and has significant acid neutralization capacity in the surficial deposits. The watershed is underlain by Precambrian greenstones, with some granite to

TABLE 1. Chemical groundwater data from Turkey Lakes Watershed ($N$ = no. of samples; CSI = calcite saturation index). Values in parentheses are standard deviations.

| Well ($N$) | Depth (m) | pH | Cond. (μmho/cm) | Alk. (μeq/L) | $Ca^{2+}$ (μeq/L) | $Mg^{2+}$ (μeq/L) | $K^{+}$ (μeq/L) | $Na^{+}$ (μeq/L) | $SO_4^{2-}$ (μeq/L) | $Cl^{-}$ (μeq/L) | CSI |
|---|---|---|---|---|---|---|---|---|---|---|---|
| HU-0.67 (76) | −0.67 | 5.01 (0.22) | 23 (3) | 15 (15) | 93 (11) | 29 (4) | 5 (4) | 24 (5) | 113 (13) | 8 (3) | $5.50 \times 10^{-7}$ |
| H1-1.81 (140) | −1.81 | 5.58 (0.25) | 25 (8) | 50 (37) | 129 (65) | 34 (10) | 4 (5) | 29 (14) | 113 (9) | 9 (13) | $1.08 \times 10^{-5}$ |
| H1-2.78 (138) | −2.78 | 6.48 (0.21) | 61 (8) | 460 (102) | 488 (67) | 81 (12) | 7 (5) | 30 (20) | 121 (19) | 9 (8) | $4.61 \times 10^{-3}$ |
| H1-3.7 (51) | −3.7 | 7.11 (0.29) | 106 (21) | 956 (48) | 943 (83) | 108 (16) | 9 (8) | 30 (12) | 135 (26) | 11 (5) | $6.34 \times 10^{-2}$ |
| W3-1 (14) | −1.2 | 5.53 (0.16) | 31 (5) | 27 (12) | 174 (18) | 40 (6) | 4 (1) | 25 (3) | 119 (17) | 6 (2) | $7.02 \times 10^{-6}$ |
| W3-2 (16) | −2.2 | 5.46 (0.12) | 33 (8) | 57 (64) | 166 (11) | 39 (4) | 4 (1) | 24 (3) | 123 (19) | 6 (2) | $1.18 \times 10^{-5}$ |
| W3-STAND (20) | −3.74 | 5.48 (0.22) | 31 (5) | 31 (15) | 166 (13) | 40 (3) | 5 (4) | 26 (3) | 122 (14) | 8 (3) | $6.84 \times 10^{-6}$ |
| W2-1 (19) | −1.35 | 5.97 (0.34) | 43 (10) | 197 (63) | 264 (65) | 63 (19) | 9 (5) | 42 (9) | 137 (17) | 8 (4) | $2.07 \times 10^{-4}$ |
| W2-2 (16) | −2.35 | 6.17 (0.16) | 41 (3) | 207 (60) | 272 (43) | 60 (8) | 7 (2) | 40 (4) | 150 (15) | 8 (3) | $3.56 \times 10^{-4}$ |
| W2-3 (18) | −3.35 | 6.11 (0.19) | 36 (2) | 144 (21) | 226 (21) | 54 (4) | 5 (1) | 38 (4) | 142 (13) | 7 (3) | $1.78 \times 10^{-4}$ |
| W2-4 (18) | −4.35 | 6.18 (0.17) | 38 (4) | 170 (47) | 235 (28) | 58 (5) | 7 (3) | 39 (4) | 148 (13) | 7 (3) | $2.58 \times 10^{-4}$ |
| W2-5 (18) | −5.35 | 6.94 (0.26) | 67 (8) | 480 (74) | 449 (73) | 105 (21) | 15 (5) | 67 (9) | 158 (22) | 7 (2) | $7.62 \times 10^{-3}$ |
| W2-STAND (21) | −6.89 | 7.17 (0.21) | 89 (11) | 619 (77) | 604 (97) | 149 (57) | 20 (5) | 84 (18) | 182 (16) | 11 (5) | $2.23 \times 10^{-2}$ |
| Surface (18) | 0 | 6.32 (0.19) | 44 (6) | 161 (57) | 289 (55) | 57 (6) | 11 (3) | 44 (40) | 136 (25) | 16 (28) | $4.13 \times 10^{-4}$ |
| W0-0.74 (28) | −0.74 | 6.19 (0.20) | 46 (6) | 195 (65) | 301 (49) | 64 (8) | 8 (3) | 54 (54) | 139 (18) | 8 (2) | $3.85 \times 10^{-4}$ |
| W0-1.25 (29) | −1.25 | 6.60 (0.24) | 65 (7) | 393 (66) | 458 (51) | 94 (22) | 7 (2) | 58 (19) | 169 (16) | 9 (3) | $2.94 \times 10^{-3}$ |
| W0-2.17 (28) | −2.17 | 6.70 (0.21) | 68 (5) | 428 (34) | 481 (37) | 104 (25) | 8 (5) | 67 (33) | 173 (11) | 9 (4) | $4.25 \times 10^{-3}$ |
| W0-2.9 (29) | −2.9 | 6.66 (0.19) | 68 (5) | 418 (28) | 497 (33) | 105 (37) | 12 (23) | 72 (61) | 169 (35) | 19 (50) | $3.89 \times 10^{-3}$ |
| W0-3.33 (18) | −3.33 | 6.85 (0.26) | 62 (14) | 422 (28) | 504 (57) | 95 (18) | 8 (5) | 67 (53) | 191 (49) | 24 (64) | $6.11 \times 10^{-3}$ |
| LTL-0.8 (7) | −0.8 | 6.71 (0.28) | 59 (5) | 283 (78) | 354 (33) | 118 (7) | 7 (2) | 51 (5) | 196 (7) | 48 (2) | $2.13 \times 10^{-3}$ |
| LTL-1.5 (9) | −1.5 | 7.62 (0.09) | 222 (16) | 2153 (130) | 1550 (232) | 408 (81) | 36 (33) | 154 (82) | 145 (20) | 12 (2) | $4.96 \times 10^{-1}$ |
| LTL-2.1 (9) | −2.1 | 7.95 (0.06) | 191 (52) | 2090 (184) | 1472 (92) | 499 (14) | 32 (4) | 237 (27) | 66 (24) | 25 (11) | $9.86 \times 10^{-1}$ |
| LTL-2.6 (9) | −2.6 | 7.97 (0.14) | 180 (13) | 1663 (69) | 1318 (111) | 355 (16) | 31 (2) | 99 (7) | 222 (5) | 11 (3) | $7.59 \times 10^{-1}$ |
| BT4-1.67 (8) | −1.67 | 7.32 (0.16) | 117 (9) | 1011 (44) | 1060 (56) | 78 (8) | 16 (5) | 44 (2) | 188 (11) | 17 (5) | $8.54 \times 10^{-2}$ |
| BT4-2.25 (10) | −2.25 | 7.59 (0.17) | 115 (7) | 899 (23) | 939 (68) | 82 (7) | 16 (3) | 50 (9) | 171 (15) | 23 (6) | $1.29 \times 10^{-1}$ |
| BT4-3.35 (8) | −3.35 | 7.59 (0.21) | 121 (9) | 1061 (12) | 1070 (111) | 86 (22) | 24 (11) | 53 (13) | 178 (19) | 13 (2) | $1.68 \times 10^{-1}$ |
| BT4-4.91 (11) | −4.91 | 8.04 (0.11) | 169 (18) | 1332 (103) | 1458 (88) | 107 (7) | 17 (5) | 59 (7) | 202 (25) | 18 (14) | $7.90 \times 10^{-1}$ |
| UD-2.45 (12) | −2.45 | 6.91 (0.19) | 59 (14) | 324 (134) | 433 (115) | 61 (14) | 9 (4) | 34 (8) | 141 (34) | 10 (4) | $4.71 \times 10^{-3}$ |
| RD-1.65 (15) | −1.65 | 6.90 (0.18) | 60 (19) | 379 (91) | 476 (82) | 66 (11) | 6 (2) | 36 (8) | 159 (19) | 9 (3) | $5.90 \times 10^{-3}$ |
| RD-2.49 (12) | −2.49 | 6.91 (0.14) | 69 (8) | 418 (106) | 511 (82) | 65 (9) | 6 (2) | 38 (6) | 157 (24) | 9 (3) | $7.07 \times 10^{-3}$ |
| RD-3.52 (10) | −3.52 | 7.09 (0.19) | 84 (7) | 551 (77) | 806 (65) | 94 (27) | 10 (6) | 61 (23) | 179 (10) | 9 (4) | $2.15 \times 10^{-2}$ |
| RD-3.69 (27) | −3.69 | 7.02 (0.24) | 80 (12) | 551 (76) | 740 (132) | 83 (24) | 7 (4) | 51 (27) | 170 (35) | 9 (4) | $1.69 \times 10^{-2}$ |
| DS-1.52 (6) | −1.52 | 6.12 (0.33) | 58 (17) | 354 (138) | 419 (162) | 88 (36) | 6 (2) | 56 (9) | 125 (34) | 10 (2) | $8.16 \times 10^{-4}$ |
| DS-1.93 (20) | −1.93 | 6.70 (0.33) | 88 (24) | 703 (114) | 783 (179) | 129 (40) | 7 (3) | 71 (33) | 163 (26) | 11 (3) | $1.10 \times 10^{-2}$ |
| DS-1.95 (16) | −1.95 | 6.69 (0.30) | 98 (12) | 729 (58) | 839 (214) | 127 (40) | 8 (4) | 77 (68) | 165 (26) | 12 (4) | $1.17 \times 10^{-2}$ |

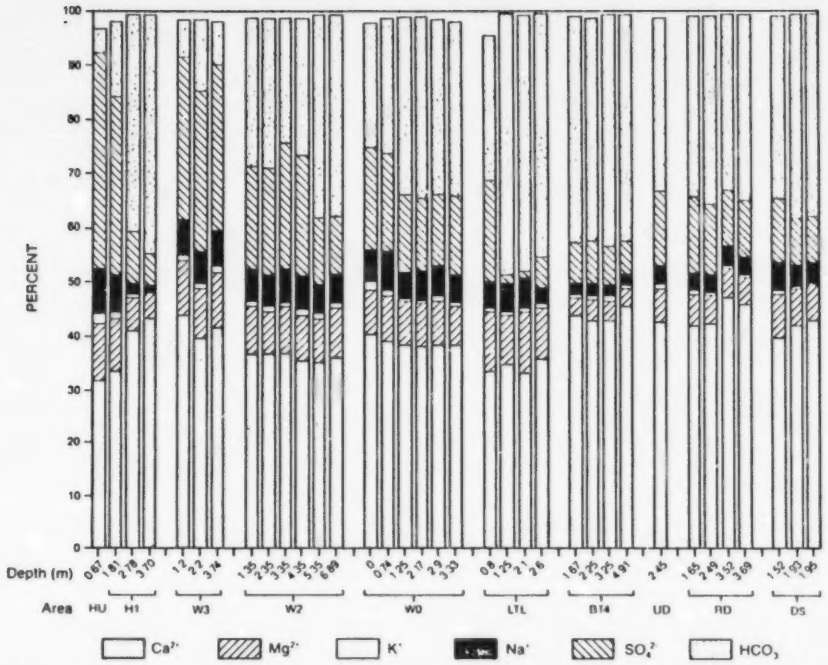


FIG. 3. Relative proportions of chemical parameters as a percentage of the total ions in the groundwater. Arrangement left to right is same as in Fig. 2.

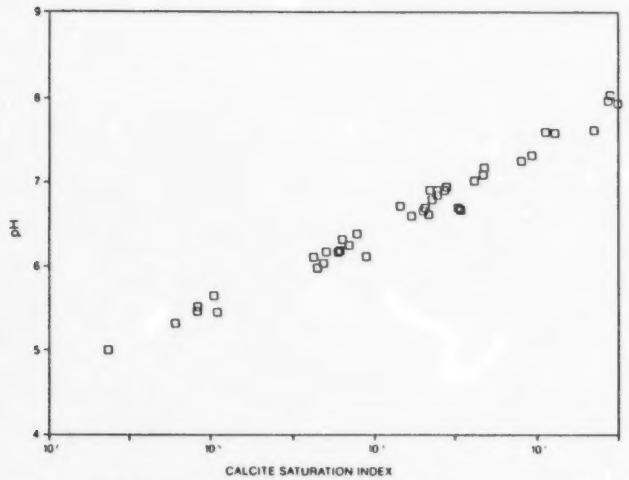


FIG. 4. Calcite saturation index versus pH for the Turkey Lakes groundwater.

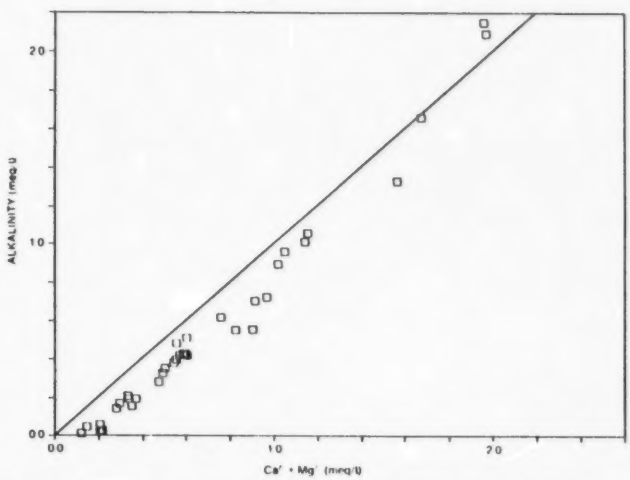


FIG. 5. Sum of $Ca^{2+}$ + $Mg^{2+}$ versus alkalinity. Note the deficit of alkalinity of approximatly 150 μeq/L. The line represent the theoretical 1:1 relationship for waters unaffected by strong mineral acids.

the northeast. Basin hydrology is partially controlled by major faults.

Much of the watershed is covered by a thin and discontinuous till. In local depressions, however, till has accumulated to a thickness of up to 70 m (Elliot 1985). The till can be divided into two types (Cowell and Wickware 1983). The upper ablation till, less than 1 m thick, has higher permeabilities ($1 \times 10^{-3}$ cm/s) and low (approaching zero) carbonate content, while the basal till has lower permeabilities ($1 \times 10^{-5}$ cm/s) and higher carbonate content (0.5–1.5%). This combination of stratigraphy and mineralogy is important to the understanding of groundwater chemistry in the Turkey Lakes Watershed.

Wells are generally located in thicker accumulations of till associated with the valley floors, but a limited number of wells (HU-0.67, W3-1, W2-1) have been constructed in the shallow till (Fig. 1). A detailed description of these wells is given in Johnston and Craig (1986). Most of the wells are in the permanent water table and produce water throughout the year. Well HU-0.67, however, produces water only during and after major infiltration events.

## Methods

Test wells were constructed using a variety of techniques, including rotary auger (least effective), percussion, and sonic vibration (most effective) (Johnston and Craig 1986).

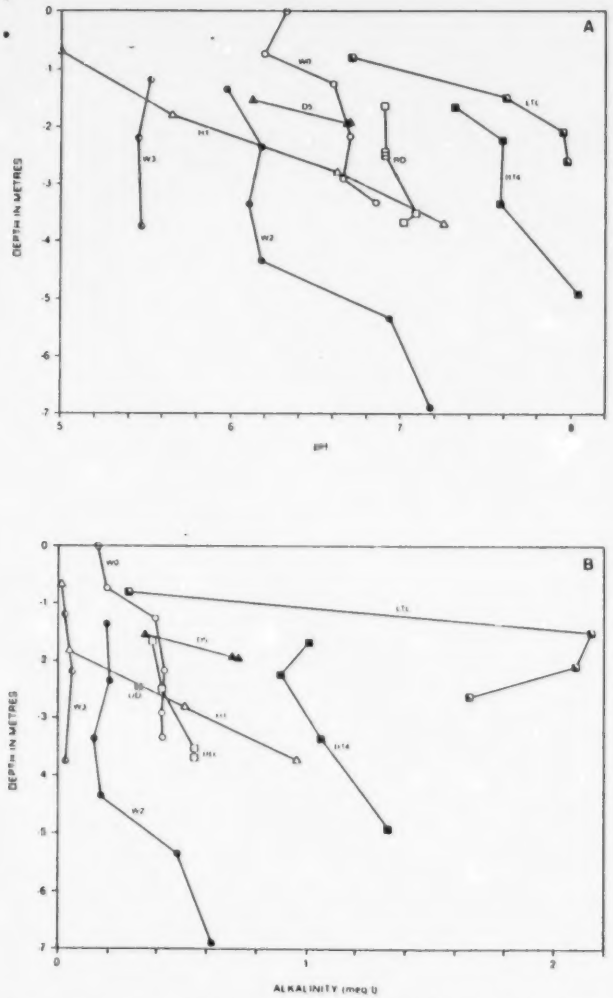


FIG. 6. (A) pH versus depth for groundwater data in the Turkey Lakes Watershed; data points connected by a line represent data from a single site. (B) Alkalinity versus depth for groundwater data in the Turkey Lakes watershed; data points connected by a line represent data from a single site.

Sample pH and specific conductance were measured in a field laboratory within an hour of sampling, and the alkalinity was measured on a filtered (0.45 μm) sample within 1 d of collection (Metrohm 682 titroprocessor). Samples were filtered (0.45 μm) and stored for the analysis of major anions (Dionex 2010i ion chromatograph) and cations in accordance with methods outlined by the Department of the Environment (1979).

## Results and Discussion

### Spatial Variation

The concentration of total ions in solution in the groundwater varies between 300 and 4500 μeq/L, a range larger than an order of magnitude (Fig. 2; Table 1). Some individual parameters have even larger ranges: the mean pH ranges from 5.0 to 8.0, alkalinity from 10 to 2200 μeq/L, $Ca^{2+}$ from 90 to 1550 μeq/L, and $Mg^{2+}$ from 20 to 500 μeq/L. The concentration of $SO_4^{2-}$ shows less variation throughout the groundwater system, ranging from 70 to 220 μeq/L. The data

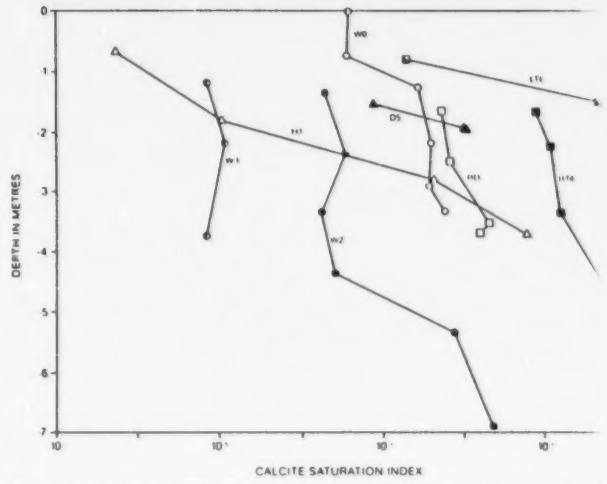


FIG. 7. Calcite saturation index versus depth; data points connected by a line represent data from a single site.

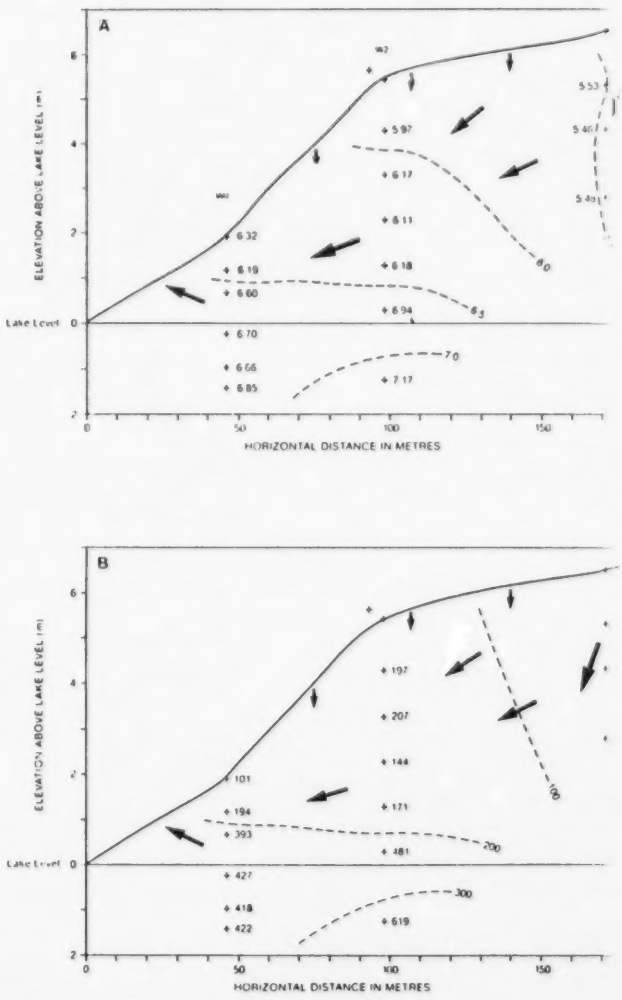


FIG. 8. (A) Changes in pH as measured along a groundwater flow system in the valley floor adjacent to Wishart Lake. (B) Changes in alkalinity as measured along a groundwater flow system in the valley floor adjacent to Wishart Lake.

in Table 1 are the means of sample data collected during all seasons, and thus the ranges contain any seasonal fluctuations.

Despite the large differences in absolute concentrations noted above, the groundwater can be divided into waters of two chemical types based on the relative importance of the $SO_4^{2-}$ and $HCO_3^-$ anions in the sample (Fig. 3). All the Turkey Lakes groundwaters sampled contain $Ca^{2+}$ as the dominant canion. One group of groundwaters has $SO_4^{2-}$ as the dominant anion. Groundwaters in this group (such as those at HU-0.67, H1-1.81, and W3) are found in recharge areas where flow is predominantly downwards. These waters are characterized by low ionic strength and low alkalinity (Table 1) and they are particularly sensitive to acid deposition. The remainder of the groundwaters are bicarbonate rich, with higher ionic strengths and alkalinities (Fig. 3). These waters are found in areas of lateral groundwater flow or discharge areas and have large buffering capacities.

The shift from $SO_4^{2-}$ to $HCO_3^-$-rich waters can be explained by the following series of reactions. In the precipitation, $SO_4^{2-}$ is the dominant anion and the $HCO_3^-$ concentration is near zero (Nicolson et al. 1987). On contact with the carbonate bearing sediments, the waters increase in $HCO_3^-$ as a result of natural weathering reactions. With further contact time and longer flow paths, the groundwater dissolves naturally occurring calcite (and minor amounts of dolomite) in the tills, which results in $HCO_3^-$ becoming the dominant anion. The variation across the watershed is due to variations in overburden chemistry and groundwater flow paths.

The degree of saturation of a given water with respect to $CaCO_3$(s) (calcite) can be determined by the ratio of the ion activity product (IAP) to the equilibrium constant ($K_{eq}$) for the reaction (Berner 1981)

$$CaCO_3(s) = Ca^{2+} + CO_3^{2-}.$$

The value of $K_{eq}$ is calculated using published constants and the IAP is determined from sample data (pH, $Ca^{2+}$, and carbonate alkalinity). The state of saturation of a natural water with regard to a specific solid is defined as follows: supersaturated (log IAP/$K_{eq} > 0$), saturated (log IAP/$K_{eq} = 0$), or undersaturated (log IAP/$K_{eq} < 0$). Supersaturated groundwater will tend to precipitate calcite, while groundwater that is undersaturated with respect to calcite will dissolve it by the reaction

$$H^+ + CaCO_3(s) = Ca^{2+} + HCO_3^-.$$

As this reaction consumes $H^+$, it results in a decrease in the acidity of the water and an increase in $Ca^{2+}$ and $HCO_3^-$ in solution. Figure 4 shows the close relationship between the calcite saturation index and pH observed in the Turkey Lakes Watershed. This relationship is consistent with the hypothesis that the weathering of calcite is the main geochemical reaction controlling groundwater $HCO_3^-$.

The calcite saturation index can also be used as a relative measure of the ability of a water to assimilate $H^+$ without undergoing a pH depression. Waters having higher values of this index will have a higher buffering capacity than those waters will lower values. Although the values of the calcite saturation index vary widely across the basin (Table 1), higher values tend to be found at lower elevations. The highest values, for example, are found around Little Turkey Lake. The increase in values seems to be related to thicker accumulations of till, and thus to longer flow paths, and to lower permeabilities, and thus longer contact times.

The chemistry of waters resulting from carbonate weathering is such that $Ca^{2+}$ and $Mg^{2+}$ should balance the $HCO_3^-$ content for waters unaffected by acidic deposition (Almer et al. 1978). This relationship was demonstrated in Sweden and several areas in Canada where lakes unaffected by acidic loadings have close to a 1:1 relationship between $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3^-]$ (in equivalents per litre) (NRCC 1981). In waters affected by acid deposition, a deficit of alkalinity (or conversely an excess of $Ca^{2+}$ and $Mg^{2+}$) should be apparent. At the Turkey Lakes the sum of $Ca^{2+}$ plus $Mg^{2+}$ plotted against $HCO_3^-$ (Fig. 5) clearly shows an average deficit of alkalinity of 150 μeq/L. The deficit represents the carbonate alkalinity utilized in neutralizing $H^+$ which is a result of strong acids in the system.

### Variation with Depth and along Flow Paths

At most sites, pH and alkalinity tend to increase with depth, but the range in concentration is usually not as large as the differences in concentration across the basin (Fig. 6). The other major parameters ($Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$) also tend to increase with depth. This pattern of increasing concentration of solutes with depth is most pronounced in recharge areas and areas of lateral flow.

A plot of the calcite saturation index (IAP/$K_{eq}$) against depth for selected wells (Fig. 7) illustrates an increase in the degree of calcite saturation with increasing depth. Almost all of the samples are undersaturated. The variation in this index from site to site within the basin is larger than the variation at any one site.

The area at the east end of Wishart Lake illustrates the changes in groundwater chemistry occurring along an assumed flow path (approximately 180 m) in a small valley. Test wells are located in the recharge area (W3), in the area of lateral flow (W2), and in the discharge area at the boundary of Wishart Lake (W0) (Fig. 8). The pH increases along the direction of the assumed flow path from approximately 5.5 in the recharge area (W3) to about 6.5 at Wishart Lake (W0) (Fig. 8A). Alkalinity (Fig. 8B) also increases, from approximately 50 μeq/L (area W3) to about 200–400 μeq/L at W0.

In general, as the groundwater moves along the flow path, the concentrations of alkalinity, $Ca^{2+}$, and $Mg^{2+}$ increase markedly. The excess of $Ca^{2+}$ and $Mg^{2+}$ relative to the alkalinity, however, extends throughout the groundwater system and is discharged to surface water and exported from the basin.

## Conclusions

The chemical concentrations in the Turkey Lakes groundwater are highly variable, especially for $Ca^{2+}$, $Mg^{2+}$, alkalinity, and pH. The concentration of $SO_4^{2-}$, while not conservative, shows less spatial variation throughout the watershed, increasing with depth at individual sites. The large spatial variations in groundwater chemistry are due to differences in permeabilities, mineralogy, and flow dynamics from site to site along a given subbasin flow system and within the entire basin.

Despite these differences and despite the large variation in chemical concentrations from site to site, the relative proportion of $Ca^{2+}$ plus $Mg^{2+}$ to alkalinity is remarkably constant across the basin. This is a result of the weathering of calcite and dolomite. Infiltrating shallow groundwaters in recharge areas can be characterized as $Ca^{2+}$–$SO_4^{2-}$ waters, and the more mature groundwaters in discharge areas can be characterized as $Ca^{2+}$–$HCO_3^-$ waters. Under present conditions the site-specific

groundwater chemistries observed in the Turkey Lakes Watershed represent stages in a continuum consisting of calcium sulfate dominated recharge waters evolving to calcium bicarbonate dominated groundwater.

It is clear, then, that the groundwater chemistry in the Turkey Lakes Watershed is controlled by carbonate-based weathering reactions. Superimposed on this is the influence of the stratigraphic configuration of sediments in the various subbasins in the watershed. In general, groundwater flow in the Turkey Lakes Watershed can be considered to be a two-layered system reflecting the stratified till structure. The upper till has fairly high permeabilities ($10^{-3}$ cm/s) and low carbonate content and the result is rapid groundwater flow characterized by low alkalinity. Water that has been confined to this upper till during its groundwater history is classified as $Ca^{2+}-SO_4^{2-}$ water. The deeper basal till has much lower permeabilities ($10^{-5}$ cm/s) and higher carbonate content. Groundwater in this layer moves approximately 100 times slower than in the surficial layer, and having much longer residence time, it is much closer to equilibrium with calcite than the faster moving groundwater in the surficial till. It is this movement through the deeper groundwater system and subsequent discharge to surface water that results in a significant movement of alkalinity from the solid mineral phase to the surface water.

We conclude that in order to determine correctly the response of the Turkey Lakes Watershed to various acid loading events, it is necessary to consider the groundwater flow as consisting of two very different pathways. This leads also to the more general conclusion that a correct evaluation of the effects of acid precipitation on a basin depends on considering the groundwater hydrology as a function of the basin stratigraphy and mineralogy. Further research is needed, however, to identify factors which determine the relative importance of the various pathways in a particular basin under different climatic conditions.

In general, groundwater in the Turkey Lakes Watershed is relatively well buffered, and discharges from the thicker (>1 m) accumulations of till provide sufficient alkalinity to ameliorate pH depressions in surface waters during acid loading events (Bottomley et al. 1984). Geochemical weathering of carbonates found in the Turkey Lakes till is the major reaction controlling groundwater alkalinity and thus, through groundwater discharge, surface water alkalinity. As a result of spatial variations in till mineralogy, till structure, and the resultant groundwater flow system, the groundwater chemistry is highly site specific.

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